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Research on the effects of tungstate and carbonate salts in green decontamination on the conversion process of 2-chloroethyl phenyl sulfide

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ABSTRACT

This article introduces the initial research results on the catalytic role of tungstate and carbonate in green decontamination (TDX-2) on the conversion process of 2-chloroethyl phenyl sulfide (CEPS is a simulant of the yperite). The result shows that, under the conditions of investigation, the catalytic ability of K_2WO_4 is about 240 times greater than that of K_2CO_3. In TDX-2, K_2WO_4 catalytically reacts about 7 times faster than K_2CO_3. The K_2WO_4 catalyst in the decontamination mixture is stable, highly durable, and less likely to cause unwanted H_2O_2 decomposition. After 18 hours of mixing, it still achieves a conversion efficiency of over 95% after 15 minutes of reaction with CEPS, while to achieve equivalent conversion efficiency, the durability of the solution with K_2CO_3 catalyst is only less than 2 hours. At the same time, K_2WO_4 limits the tendency to over-oxidize sulfide to sulfone compared to K_2CO_3.

Introduction

In the military context, decontaminants represent substances or mixtures capable of converting contaminants into non-contaminant or less contaminating compounds. Decontaminants containing chlorine, such as hypochlorite, chloramine,... are highly effective with affordable price. However, they normally pose certain threats to human well-being, the environment, weaponry, and storage facilities [1]. Subsequently, the storage and utilization of chlorine-based decontaminants have been widely restricted. In recent decades, green chemistry (also known as clean chemistry, environmental chemistry, benign chemistry or sustainable chemistry) has emerged as a new development trend in both civilian and military domains. The environmental friendliness of chemical compounds is classified into three levels: edible, touchable, and usable in agriculture and industry.

H_2O_2 is considered an ideal oxidant, exhibiting an atom economy of 47% with the sole byproduct of water, which is widely available, and safe for storage, transportation and use. It exhibits strong oxidative capacity, especially when combining with appropriate catalytic activators. Generally, H_2O_2 catalytic activators are classified into four groups, namely organic activators, metal ion activators, metal complexes (biomimetic), and metal salt activators [2]. It is important to note that transition metal salt activators are of particular interest because of their uniqueness and robust catalytic potential. Some authors have studied the oxidation ability by H2O2 such as: Yang Li studied the oxidation of active hydrogen peroxide by carbonate to remove organic pollutants from highly alkaline wastewater [3], Ian A. Fallis studied

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H_2O_2/K_2WO_4 to oxidize HD and some simulants [2], Nguyen Thi Thuy used H_2O_2/K_2WO_4 to oxidize soybean oil [4]. Based on these principles, the composition of individual components of green decontaminants (TDX-2) has been developed and published, including H_2O_2 as the oxidizer, K_2WO_4 (0.005 M) as the catalyst, K_2CO_3 (0.15 M) as a co-catalyst and alkalinity regulator, a buffer, and the organic solvents [5]. To clarify the impact of K_2WO_4 and K_2CO_3 on the conversion rate, conversion trends, and the durability of the TDX-2 compounds, two decontaminating systems were investigated, including: K_2WO_4/H_2O_2/organic solvent and K_2CO_3/H_2O_2/organic solvent. The converting substance is 2-chloroethyl phenyl sulfide (CEPS), a simulant for chemical warfare agents yperit with the toxic core being the sulfur atom and chloroethyl group. When at least one functional group is destroyed, the level of skin burning is significantly lowered [1]. Therefore, the objective of the reaction is to break down these cause of toxicity to eliminate or reduce the toxicity of the compound.

Experimental

Reagents

CEPS (98%, Sigma Aldrich); H_2O_2 (30 %); Merck; TX-100 (99%); Propylene Carbonate-PC (99%); propylene glycol-PG (99%); K_2WO_4 (99%), K_2CO_3 (99%), Na_2CO_3 (99%), Na_2SO_3 (99%): Macklin; chloroform, methanol for HPLC (Fisher); single-distilled water (Vietnam), and other standard laboratory chemicals.

Apparatus

High Performance Liquid Chromatography (HPLC) Agilent HP-1100 (USA) with a C8 column (250 mm x 4.6 mm x 5 µm), and UV-VIS Diode Array Detector (DAD) with a scanning range of 0-1100 mm; Gas Chromatography-Mass Spectrometry (GC-MS), Agilent 5975 (USA) with a DB-5MS column (30 m × 0.32 mm × 0.25 mm).

Research methods on the conversion process of CEPS

The experiments were conducted within 10 mL test tubes with lids as follows: add 100 µL TX-100, 100 µL PC, and 200 µL PG solvents sequentially [5]; next, the investigated decontaminating components were put into the test tubes to the volume of 1mL; introduce 20 µL CEPS into the test tubes (with the decontaminants : CEPS ratios of 50:1 by volume). After that, a vortex mixer was applied at a speed of 1800 rpm for 30 seconds to ensure homogeneity. At specific time intervals, a 59 µL sample was withdrawn and added to a test tube containing 1 mL of a reaction-stopping solution composed Na_2SO_3 0.2 M and Na_2CO_3 0.2 M, before being well-mixed. Subsequently, 2 mL of chloroform was then added, and the mixture was shaken for 2 minutes to extract the chloroform layer. This solution was then filtered via a 0.22 µm membrance filter and analysed using HPLC to identify the CEPS concentration.

Analytical method CEPS using HPLC

The CEPS concentration at each designated time interval was analysed using HPLC method with the following experimental conditions: Detection wavelength: 220 nm; Mobile phase: Methanol/water (V/V) = 70/30; Flow speed: 1mL/minute; Injection volume: 10.0 µL; Retention time for the HD peak: tr = 6.286 minutes.

Research methods on identifying the conversion products using GC-MS

The chloroform extracts after being dried by using anhydrous Na_2SO_4 were filtered via a 0.22 µm membrane filter and analysed through GC-MS to determine CEPS and other conversion products. The analytical conditions were as follows: Carrier gas: Helium; Initial temperature: 40°C, maintained for 1 minute; Final temperature: 280°C, maintained for 5 minutes; Heating rate: 10°C /minute. Compounds were identified by comparing the mass spectra of the analytes with the NIST spectral library and using the fragment matching method [5].

Results and discussion

The influence of tungstate and carbonate salts on the CEPS conversion efficiency and rate

In the military, the speed and conversion efficiency of decontaminants are the key factors to ensure the rapid and thorough treatment of the toxic agents. To examine the role of K_2WO_4 và K_2CO_3 in the formulation of TDX-2 in the CEPS conversion, six experiments were conducted: system 1 - K_2WO_4/ H_2O_2 4.32 M/organic solvent; system 2 – K_2CO_3/H_2O_2 4.32 M/organic solvent. Specifically, in system 1, K_2WO_4 was studied at three concentrations: 0.001 M, 0.0025 M, and 0.005 M. In System 2, K_2CO_3 was examined at concentrations of 0.05 M, 0.15 M, and 0.5 M. The results are shown in Figure 1.

As seen from Figure 1a, overall, system 1 – at a very low concentration – the reaction proceeding rapidly with the K_2WO_4 0.005 M, the CEPS conversion efficiency achieved 98.88% after 10 minutes of reaction. Meanwhile, system 2 – the reaction happening slower with the K_2CO_3 0.15 M, the conversion efficiency reached 34.00% and 46.38% after 10 minutes and 15 minutes of reaction, respectively, which subsequently increased to 91.75% after 60 minutes of reaction. To achieve a CEPS conversion efficiency comparable to K_2WO_4 0.0025 M, a K_2CO_3 concentration of 0.5 M was required.

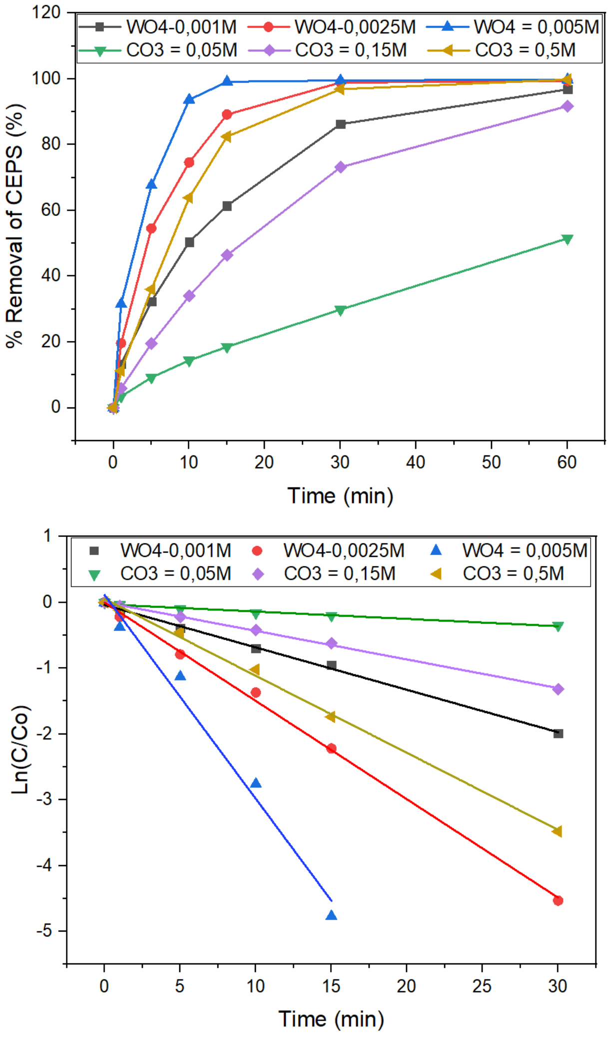

Fig. 1: The influence of K_2WO_4 and K_2CO_3 on the kinetics of CEPS conversion

Simultaneously, the results shown in Figure 1b. indicate that, at the investigated concentration conditions, the value of ln(C/Co) linearly decreased over time (t). Thus, the CEPS conversion reaction follows a pseudo-first-order kinetic model. During this period, the conversion rate constant k is calculated as follows [6]:

$$C_t/C_o = \exp(-Kt) \qquad (1)$$

The half-life of CEPS ($t_{1/2}$) is calculated using the following formula:

$$t = t_{1/2} = \ln 2/K = 0.693/K \qquad (2)$$

The K/C ratio was used to compare the catalytic performance of K_2WO_4 and K_2CO_3. The kinetic parameters of the reaction are subsequently determined, as summarized in Table 1.

Table 1. Kinetic parameters of the CEPS conversion reaction

Reaction system	Rate Constant K (min−1)	Correlation Coefficient R^2	Half-life $t_{1/2}$ (minutes)	K/C ratio
K_2WO_4 = 0.001 M	0.0643	0.9972	10.78	64.30
K_2WO_4 =0.0025M	0.1495	0.9983	4.64	59.80
K_2WO_4 = 0.005 M	0.2892	0.9846	2.40	57.84
K_2CO_3 = 0.05 M	0.0114	0.9837	60.79	0.23
K_2CO_3 = 0.15 M	0.0434	0.9986	15.97	0.29
K_2CO_3 = 0.5 M	0.1169	0.9972	5.93	0.23

As seen from Table 1, the K/C ratio in system 1 ranges from 57.84 to 64.30, while the ratio in system 2 fluctuates between 0.23 and 0.29; which means the ability of K_2WO_4 to activate H_2O_2 under the investigated conditions is approximately 240 times stronger than that of K_2CO_3. Regarding TDX-2, at a K_2WO_4 concentration of 0.005 M, the reaction rate constant is about 7 times higher than that with K_2CO_3 at 0.15 M.

This can be explained as follows: In the aqueous phase, the catalytic precursor K_2WO_4 is rapidly oxidized by H_2O_2 to form the bisperoxowonfram complex, according to the equation [4, 7]:

$$K_2WO_4 + 2H_2O_2 \rightarrow K_2[WO(O_2)_2(OH)_2] + H_2O \qquad (3)$$

The peroxo complexes possess strong oxidative capacity, allowing it to approach and oxidize sulfide. Simultaneously, K_2CO_3 is also able to combine with H_2O_2, creating peroxo complex HCO4- with significantly stronger oxidative properties than H_2O_2 alone [3]:

$$CO_3^{2-} + H_2O \leftrightarrow HCO_3^- + OH^- \qquad (4)$$

$$HCO_3^- + H_2O_2 \leftrightarrow HCO_4^- + H_2O \qquad (5)$$

Besides the impacts of kinetic factors, several other factors also influence the conversion process, such as: the motion rate of molecules, spatial effects, phase-transferring capability of the peroxo complex,... The above-mentioned factors exhibit pivotal contributions to the superior catalytic role of K_2WO_4 compared to K_2CO_3.

The influence of tungstate and carbonate salts on the durability of green decontamination systems.

As for decontaminants used in military context, it is necessary to prepare the mixture several hours in advance. Therefore, apart from the conversion rate and efficiency, the durability after being mixed is of paramount significance.

To examine the durability of the decontamination systems, the time range studied was from 0 to 18 hours. The difference was clearly demonstrated via six experiments: two experiments were conducted with system 1 being K_2WO_4 0.005 M /H_2O_2 4.32 M, with the reactions happening immediately and after 18 hours of being mixed and stored at room temperature. Four experiments were implemented with system 2 being K_2CO_3 0.15 M/H_2O_2 4.32 M and K_2CO_3 0.5 M/H_2O_2 4.32 M, with the reactions occurring promptly and after 02 hours of being mixed and maintained at room temperature.

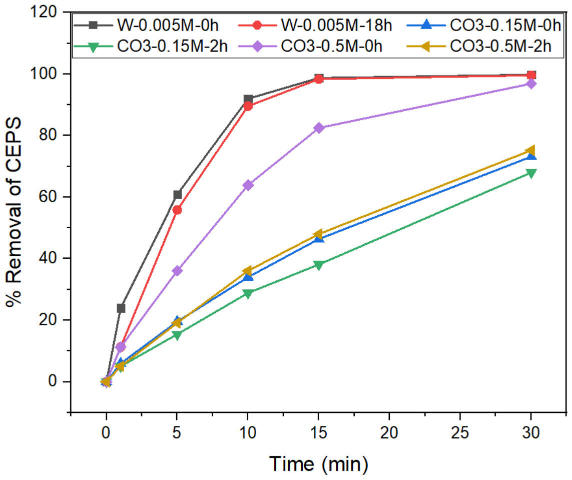

Figure 1. The effect of mixing time on CEPS conversion efficiency

From Figure 2, it can be observed that, in system 1, the decontaminants utilized either right after the mixing process or over 18 hours produce an exceptionally high efficiency, with the rate being 97% after 15 minutes. This indicates that system 1 exhibits not only high efficiency but also noticeable level of durability. Meanwhile, system 2 with K_2CO_3 0,15 M/H_2O_2 4.32 M displays comparable durability after 2 hours of mixing. However, the efficiency rate was relatively low, recording 48% after 15 minutes of reaction. The K_2CO_3 0.5 M/H_2O_2 4.32 M system reveals that the instant use subsequently leads to the efficiency rate reaching 82.5% within 15 minutes of reaction. This is due to the bisperoxowonfram complex possessing strong oxidative properties while being chemically stable, preventing the conversion process under decontaminating condition and the inefficient decomposition of H_2O_2 [8]. In contrast, the peroxo complex HCO_4^-, with stronger oxidative properties than H_2O_2, at high concentration of K_2CO_3, displays low level of durability, causing the decomposition and generation of O_2 gas bubbles.

The influence of tungstate and carbonate salts on the product formation trend in the conversion process.

As the toxic cores of yperite toxic agent lies in the sulfur atom and the chloroalkyl group, the ultimate goal of decontamination process is to oxidize the S atom to convert it into less toxic compounds, creating sulfoxide – a product with low level of toxicity and does not cause skin burns. Simultaneously, it is crucial to control the excessive oxidation, leading to the formation of sulfone, which possesses high toxicity [9, 10]. To determine the influence of tungstate and carbonate salts on the formation trend of CEPS conversion products, two experiments were conducted with system 1: K_2WO_4 0.0025 M/H_2O_2 4.32 M and K_2WO_4 0.01 M/H_2O_2 4.32 M; two experiments were conducted with system 2: K_2CO_3 0.15 M/H_2O_2 4.32 M and K_2CO_3 0.5 M/H_2O_2 4.32 M.

The CEPS conversion products were identified using GC/MS. The GC chromatogram detects 7 peaks with specific retention time of 14.352 minutes; 14.492 minutes, 15.592 minutes, 16.956 minutes, 18.321 minutes, 18.539 minutes and 18.736 minutes. Based on characteristic ion fragments on MS spectra shown in Figure S1, coupled with the comparison with the NIST library, the substances corresponding with these peaks are identified. In details, peak 1 is 2-chloroethyl phenyl sulfide (with the m/z values of ion fragments of 77, 109, 123, 172; match score of approximately 98%); Peak 2 is ethenylsulfinyl benzene (with the m/z values of ion fragments of 77, 104, 125, 152; match score of approximately 95%); peak 3 is ethenylsulfonyl benzene (with the m/z values of ion fragments of 77, 104, 125, 168; match score of approximately 97%); peak 4 is methyl phenyl sulfone (with the m/z values of ion fragments of 65, 77, 78, 141, 156; match score of approximately 96%); peak 5 is methylsulfinyl benzene (with the m/z values of ion fragments of 77, 109, 125, 172; match score of approximately 94%); peak 6 is 2-chloroethyl sulfonyl benzene (with the m/z values of ion fragments of 63, 77, 125, 141, 204; match score of approximately 95 %); peak 7 is 2-phenylsulfonyl ethanol (with the m/z values of ion fragments of 77, 109, 125, 141; match score of approximately 97%). Among these, Peak 2 and peak 5 represent the sulfoxide group, while Peaks 3, 4, 6, and 7 belong to the sulfone group.

To identify the product formation process, samples from System 1 were analyzed by GC/MS after 15 minutes of reaction, and samples from System 2 after 60 minutes of reaction, when CEPS had been converted by over 90%. The GC chromatogram results are presented in Figure S2 in the Appendix section.

From Figure S2 in the Appendix and Table 2, increasing the catalyst concentration generally enhances the formation of undesirable sulfone products. As for system 1, the rise in the concentration of K_2WO_4 from 0.0025 M to 0.01 M further leads to the decrease in the sulfoxide proportion from 77.59% to 56.66% while the sulfon proportion increases from 22.41% to 43.34%. Meanwhile, in System 2, product ratios change rapidly; at 0.15 M K_2CO_3, the sulfoxide proportion was 57.81% and the sulfone proportion was 42.19%. When the K_2CO_3 concentration was raised to 0.5 M, sulfoxide was almost entirely converted to sulfone.

This phenomenon can be explained as follows: the oxidization process undergoes two distinct phases with the first phase being the conversion of sulfur into sulfoxide, and the second phase being the oxidation of sulfoxide into sulfone. Regarding system 1, the bisperoxowonfram complex exhibits strong oxidative properties but inclines to cease in the first phase, favoring sulfoxide formation and minimizing over-oxidation to sulfone. In contrast, in System 2, the peroxo HCO_4^- complex tends to favor excessive oxidation, leading to sulfone formation.

Therefore, although the increase in the catalyst concentration strengthens the oxidative properties of the decontaminants, it also leads to the formation of undesirable sulfone products. In the proposed TDX-2 solution with the concentration of 0.005 M K_2WO_4 and 0.15 M K_2CO_3, the formulation achieves a balance by accelerating CEPS conversion while restricting sulfone formation.

Table 2. The peak height and the relative percentage ratio of sulfoxide and sulfone products

Reaction system	h Peak 2	h Peak 3	h Peak 4	h Peak 5	h Peak 6	h Peak 7	% Sulfoxide	% Sulfone
K_2WO_4 0.0025M	10^4	$45x10^3$	$5x10^4$	$44x10^4$	10^4	$25x10^3$	77.59	22.41
K_2WO_4 0.0100M	$6x10^3$	$95x10^3$	$15x10^4$	$36x10^4$	10^4	$25x10^3$	56.66	43.34
K_2CO_3 0,15M	10^3	$35x10^3$	$19x10^4$	$36x10^4$	$5x10^2$	$38x10^3$	57.81	42.19
K_2CO_3 0,5M	0	0	$29x10^4$	0	0	$9x10^4$	0	100

Conclusion

The influence of tungstate and carbonate salts in TDX-2 on the CEPS conversion process studied indicates that: under the investigation conditions, the catalytic ability of K_2WO_4 is about 240 times greater than that of K_2CO_3. In TDX-2, the CEPS conversion role of tungstate is about 7 times greater than carbonate. Simultaneously, the tungstate catalyst possesses higher level of durability, while restricting the excessive oxidation of sulfide into sulfone.

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